

METHOD OF BONDING A POLYMER SURFACE TO A CONDUCTIVE OR
SEMICONDUCTIVE SURFACE AND ITS APPLICATIONS

DESCRIPTION

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Technical Field

The present invention relates to a method for bonding a
polymer surface to a conductive or semiconductive
10 surface, to applications of this method and to
structures obtained by implementing it.

The term "polymer surface" is understood to mean a
surface formed from a polymer and corresponding to all
15 or part of the surface of an object that may be either
exclusively made from this polymer or formed from one
or more other materials, at least one part of the
surface of which consists of said polymer. In
particular, the object may be an object that includes
20 an electrically conductive or semiconductive region,
the surface of which consists of a polymer.

The expression "conductive or semiconductive surface"
is understood to mean a surface consisting of an
25 electrically conductive or semiconductive material and
corresponding completely or partly to the surface of an
object that may be either exclusively formed from this
conductive or semiconductive material or is formed from
one or more other materials, at least one part of the
30 surface of which consists of said conductive or
semiconductive material.

The method according to the invention is of course
applicable in all fields in which it is necessary to

bond a polymer, and in particular a thermoplastic polymer, to an electrically conductive or semiconductive surface.

5 For example, mention may be made of the field of composites, such as those used in the aerospace, aeronautical and automotive industries in which the problems of corrosion-protection paints and coatings on parts flaking off for example can be remedied by the
10 method of the invention. Mention may also be made of the biomedical field in which the method according to the invention may be useful, for example, for coating medical or implantable surgical instruments such as vascular endoprostheses (or stents), aneurysm guides,
15 catheter guides, pacemakers, hip prostheses, cochlear implant electrodes, dental implants or even electrophysiology electrodes, with biocompatible materials suitable for ensuring controlled release of biologically active substances.

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However, the method according to the invention may also be applicable in fields where it is necessary for there to be strong mechanical attachment between two objects having electrically conductive or semiconductive
25 regions, and especially when the attachment has to be effected in these regions. In particular, the method according to the invention may be of great use in the case in which it is desirable for the attachment to be carried out at temperatures below those needed for
30 effecting direct thermal bonding, whether for technical reasons (such as the heat sensitivity of the materials) or economic reasons, or else when the attachment is intended to be carried out via a flexible link. Such constraints are very commonly present in the assembly

of sensitive components of microsystems, such as microsensors, and in particular in the assembly carried out using the PFC (polymer flip chip) technology.

5 Prior Art

The bonding of an organic material, and especially a polymer, to an electrically conductive or semiconductive material poses a number of difficulties.

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This is because organic materials exhibit localized surface states: in chemical terms, they are said to possess functional groups. In this context, it is "simple" to carry out chemistry on a polymer surface insofar as this involves making the functional groups react together and therefore draws on experience acquired in organic chemistry. However, the surface of conductive or semiconductive materials is formed from delocalized electronic states (excluding surface defects): in chemical terms, even the notion of functional groups disappears and experience acquired in organic chemistry can no longer be applied to the surface chemistry of conductive or semiconductive materials.

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Thus, included among the proposed solutions are firstly those consisting in providing the surface of the conductive or semiconductive material with organic functional groups so that this material can be bonded to the organic material by a chemical reaction.

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This may for example be achieved by forming, on this surface, layers of oxides or hydroxides on which it is then possible to make complementary functional groups.

react, such as isocyanate groups (EP-A-1 110 946 [1]), siloxanes (WO-A-00/51732 [2]) or acid chlorides (FR-A-2 781 232 [3]), or using bifunctional coupling agents or chemical adhesion promoters such as
5 γ -aminopropyltrimethoxysilane (E.P. Plueddmann in "Fundamentals of Adhesion", L.H. Lee (Editor), page 269, Plenum Press, New York, 1990 [4]).

The surface of the conductive or semiconductive
10 material may also be pretreated so as to create functional groups thereon that have a higher reactivity than that of the abovementioned oxides and hydroxides, with a view to obtaining a more rapid reaction with the polymer material. These may especially be unstable
15 functional groups, formed in a transient manner, such as radicals generated by an abrupt oxidation of said surface, either by chemical means or by irradiation.

Thus, for example, US-A-6 022 597 [5] proposes the
20 exposure of the surface to a reactant having nitrogen-generating groups (for example azide groups) and bombardment of this surface by particles (ions, electrons, protons, etc.) in order to convert the nitrogen-generating groups into nitrene groups capable
25 of subsequently reacting with a large number of organic functional groups.

Patent US 6 287 687 [6] proposes the functionalization
of a surface by subjecting it to a plasma treatment in
30 which the plasma gas contains a monomer capable of polymerizing or copolymerizing with other compounds that can polymerize under irradiation.

Patent US 4 421 569 [7] proposes to functionalize a surface by applying an aqueous suspension, comprising a polymer precursor monomer, a prepolymer, metal salts and a catalyst, to said surface, the metal salts being
5 used to oxidize said surface so as to create thereon radicals that can initiate the monomer and prepolymer polymerization reactions.

The surface of the conductive or semiconductive
10 material may also be functionalized by means of radicals that are made to react by irradiation with heavy ions (US A-6 306 975 [8]), by thermal means (WO-A-98/49206 [9]) or even photochemically as disclosed in WO-A-99/16907 [10].

15 All these methods rely on the intention of creating the strongest possible chemical bonds, and especially covalent bonds, at the organic material/conductive or semiconductive material interface. In general, these
20 methods have the two disadvantages of using chemical reactants and/or activation operations that are complex and expensive, and of requiring the optimization of operating protocols that are often lengthy, since the surface chemical reactions occur at substantially lower
25 rates than equivalent rates in solution.

Moreover, methods using polymerization reactions initiated from the surface of a material make it possible, at the end of reaction, to remove neither the
30 initiators nor certain monomers that have not reacted. Now, many of these compounds are toxic, because they are reactive, which makes this type of method unsuitable for use in the biomedical field.

In addition, insofar as the material that has to be attached to the functional groups provided on the surface of the conductive or semiconductive material itself acts as a chemical reactant, it is often
5 necessary to chemically modify said material in order to attach to it groups that are complementary to those present on said surface. This again adds, to the operating protocols, at least one additional step and substantially increases its cost.

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Another type of solution consists not in creating chemical bonds at the organic material/conductive or semiconductive material interface but in forming, on the conductive or semiconductive surface, a layer of
15 the organic material, which is insoluble in most known solvents, by reckoning on the fact that physical forces present are sufficient to ensure adhesion of this organic material to said surface, as long as the interface is stable.

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This can be achieved in particular by crosslinking the organic material during or after its deposition on the surface of the conductive or semiconductive material, it being possible for this deposition to be carried out
25 by spin coating or by dip coating.

This approach is used in the biomedical field, for example for coating stents with polymeric reservoirs of active molecules, which are subsequently stabilized by
30 crosslinking of fibrin (EP-A-0 701 802 [11]) or of a chemical crosslinking agent (WO-A-98/32474 [12]), and in the field of microsystems for producing polymer bumps used for the mechanical assembly of microstructures via the PFC technology, or else used

for the encapsulation of Microsystems (US-A-6 335 571 [13])).

5 However, this approach has the major disadvantage of
resulting, owing to the absence of bonds at the
interface between the organic material and the
conductive or semiconductive material, in joints that
are mechanically not very strong, especially when they
are subjected to stresses of the vibration, torsion or
10 similar type, in particular at the organic
material/conductive or semiconductive material
interface.

Even though the PFC technology has developed
15 considerably, many assemblies are still produced using
the "indium bump or flip-chip connection" technique
that uses fusible metal bumps based on lead and indium
(FR-A-2 780 200 [14]). In general, this type of
assembly requires high bonding temperatures and also
20 uses mechanically weak joints because they can break
when stressed.

Finally, it should be emphasized that, in the case of
the assembly of microstructures, none of the
25 abovementioned methods is suitable for use in
restricted conductive or semiconductive regions. This
is because, whether attachment is via chemical surface
reactions, crosslinked polymers or fusible bumps, it is
necessary in all cases, during at least one step, to
30 carry out a conformal deposition process, in which the
material deposited conforms to the topology of the
conductive or semiconductive regions, such as the use
of dispensing robots capable of pipetting a polymer
solution at the desired point or else laser ablation

operations capable of removing a layer of polymer that has been uniformly deposited on the surface.

5 It follows from the foregoing that there exists a real need for a method that allows a polymer material to be firmly attached to a conductive or semiconductive surface while being free of the drawbacks of the various methods proposed hitherto for carrying out such an attachment.

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Summary of the Invention

The present invention makes it possible to meet this requirement by providing a method of bonding a polymer
15 surface to a conductive or semiconductive surface, which method is characterized in that it comprises:

- a) the electrografting of an organic film onto the conductive or semiconductive surface, and then
- b) an operation of bonding the polymer surface
20 to the conductive or semiconductive surface thus grafted.

Within the context of the present invention, the expression "electrografting of an organic film onto a
25 conductive or semiconductive surface" is understood to mean an operation that consists in bringing this surface into contact with at least one precursor of this organic film and in causing, by applying one or more electrical potential scans to the conductive or
30 semiconductive surface, this precursor to be attached via covalent bonds to said surface and, thereby, forming an organic film.

The attachment of the precursor to the conductive or semiconductive surface may, when said precursor lends itself thereto, be accompanied by precursor polymerization reactions that have the effect in particular of increasing the thickness of said organic film.

Moreover, the expression "operation of bonding a polymer surface to a conductive or semiconductive surface" is understood to mean an operation consisting in bonding these two surfaces so that they form an indivisible mass.

As will be described later, this operation may be carried out equally well cold, for example by means of a substance capable of dissolving or swelling the polymer surface and the organic film electrografted onto the conductive or semiconductive surface - this type of operation being referred to hereafter by the term "cold bonding" - as hot, i.e. by supplying thermal energy suitable for causing the contacting surfaces to melt - this type of operation being called hereafter "hotmelt bonding", or even by combining cold bonding with hotmelt bonding.

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Before carrying out this bonding operation, the method according to the invention includes subjecting the conductive or semiconductive surface to a pretreatment, which consists of the electrografting of an organic film, the film thus electrografted having the two advantages of being highly adherent to the surface that has given rise to it and of being organic, like the polymer surface that has to be bonded to the conductive or semiconductive surface.

Thus, although the thickness of this film is generally small to very small (i.e. less than 1 μm or even less than 500 nm), it turns out, surprisingly, that said
5 film is capable of acting as a bonding "seed" and of making it possible to form a bonded joint between the conductive or semiconductive surface and a polymer surface by simple contact between the latter and by applying bonding conditions.

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Thus, although it is impossible ordinarily to bond a polymer material directly to a conductive or semiconductive material, owing to their difference in nature and, thereby, difference in melting points,
15 difference in bonding stresses, etc., such bonding is made possible by the method according to the invention thanks to a prior modification of the surface of the conductive or semiconductive material, this modification consisting in the electrografting of an
20 organic film.

According to the invention, the organic film may be electrografted onto the conductive or semiconductive surface by electroinitiated grafting or
25 electrocontrolled deposition, in which case the organic film is a polymer film.

In the case of electroinitiated grafting, it is only the attachment of the precursor to the conductive or
30 semiconductive surface that results from an electrochemical reaction, that is to say a reaction caused by the application of an electrical potential, the precursor polymerization reactions, when they

exist, being purely chemical, autonomous and independent of any electrical potential.

However, in the case of electrocontrolled deposition,
5 the precursor polymerization reactions are electrochemical, like the attachment of this precursor to the conductive or semiconductive surface, and therefore remain bonded by maintaining an electrical potential. An example of electrocontrolled deposition
10 is electropolymerization that uses, as precursors, conductive monomers such as pyrrole, aniline, thiophene or EDOT (ethylene dioxythiophene).

Within the context of the present invention, it is
15 preferred that the electrografting of the polymer organic film be electroinitiated grafting. This is because the inventors have found that this type of electrografting has the following advantages: (i) it results in the formation of covalent bonds between the
20 polymer organic film and the conductive or semiconductive surface; (ii) it allows polymer to be deposited extremely locally on chosen areas having a given work function; (iii) it permits very precise control over the thickness uniformity, even on highly
25 uneven ohmic-drop topographies (rough surfaces, worked surfaces having high aspect ratio features, etc.).

According to a first preferred way of implementing the method according to the invention, when the organic
30 film is a polymer film, the precursor is a monomer or a precursor prepolymer of this film, or else a mixture of the two.

In this preferred method of implementation, the electrografting of the polymer film comprises, apart from the attachment of the precursor of this film to the conductive or semiconductive surface, polymerization reactions within the chain of this precursor. These polymerization reactions take place from the monomers and/or prepolymers that are attached to said surface under the effect of the electrical potential, and results in growth or "sprouting" of polymeric chains from this surface. Each polymeric chain thus formed is therefore covalently bonded to the conductive or semiconductive surface.

When the grafting is electroinitiated, the precursor monomers and prepolymers of the organic film may be chosen, in the first place, from organic compounds having vinyl groups, in which case the electroinitiation consists of an electroreduction (or an electrooxidation) of these monomers and/or prepolymers. It is these thus electroreduced (or electrooxidized) monomers and/or prepolymers that initiate the polymerization reactions which, in this case, are anionic (or cationic).

The monomer compound or prepolymer that can be used for this purpose is partly or completely functionalized by vinyl groups, and especially vinyl monomers such as acrylonitrile, methacrylonitrile, acrylates and methacrylates (methyl acrylate and methyl methacrylate, ethyl acrylate and ethyl methacrylate, propyl acrylate and propyl methacrylate, butyl acrylate and butyl methacrylate, hydroxyethyl acrylate and hydroxyethyl methacrylates, glycidyl acrylate and glycidyl methacrylate; polyethylene glycol dimethacrylate,

polydimethylsiloxane acrylate and polydimethylsiloxane methacrylate), acrylamides and methacrylamides, cyanoacrylates, acrylic acid and methacrylic acid, styrene, vinyl halides, N-vinylpyrrolidone, 2-vinylpyridine, 4-vinylpyridine and vinyl-terminated telechelic compounds.

When the grafting is electroinitiated, the monomers and prepolymers may also be chosen from organic compounds containing cyclic groups that can be cleaved by nucleophilic or electrophilic attack, in which case the electrografting takes place according to the same principle as that above apart from the fact that the growth of the polymeric chains results from opening the monomer or prepolymer rings.

In this case, any monomer or prepolymer compound partly or completely functionalized by cyclic groups cleavable by nucleophilic or electrophilic attack can be used, especially epoxides, ϵ -caprolactone, butyrolactone and telechelic compounds having cleavable cyclic end groups.

According to another preferred way of implementing the method according to the invention, the precursor of the organic film is chosen from diazonium salts, especially aryl diazonium salts, sulfonium salts, phosphonium salts, iodonium salts and mixtures thereof, these salts preferably being functionalized by macromolecular fragments of the polyethylene and other polyolefin or polyethylene oxide type, and more generally any thermoplastic oligomer or polymer.

These salts have in common the fact that their reduction results in radicals that are adsorbed on the conductive or semiconductive surface and cause no growth of polymeric chains. This is therefore one particular case of electroinitiated grafting, in which the latter is reduced to its simplest expression and allows films of very small thickness, close to a molecular monolayer, to be produced.

10 According to the invention, it is also possible to carry out the electrografting of the organic film by using several precursors chosen from the various types of precursors mentioned above.

15 Be that as it may, the electrografting of the organic film is preferably obtained by immersing the conductive or semiconductive surface in a solution containing the precursor or precursors of said organic film and by connecting this surface to a potentiostat so as to
20 apply one or more electrical potential scans to it, these scans possibly being continuous or discontinuous, sinusoidal or pulsed scans.

Once the organic film has been electrografted, the
25 operation of bonding the polymer surface to the conductive or semiconductive surface may be carried out, this preferably consisting of a hotmelt operation or a cold bonding operation or else a hotmelt/cold bonding combination.

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The hotmelt operation may be carried out by applying one surface to the other and supplying, to the resulting assembly, optionally in a press or clamped, thermal energy, for example by heating or by applying

electromagnetic radiation, sufficient to melt the two contacting surfaces and thereby causing them to interpenetrate.

- 5 Sufficient thermal energy corresponds, for example, to a temperature above that one which, of the glass transition temperatures of the polymer surface that has to be bonded and of the organic film electrografted onto the conductive or semiconductive surface, is the
10 higher.

As regards the bonding, it is preferred to use, as bonding agent, a substance, for example a solvent, that is capable of both dissolving or swelling the polymer
15 surface that has to be bonded and the organic film electrografted onto the conductive or semiconductive surface.

This bonding may be accomplished in various ways
20 depending on its end use. Thus, for example, if the purpose of the bonding is to coat a polymer onto a part made of a conductive or semiconductive material and able to withstand being subjected to an immersion operation - which is especially the case for a stent or
25 a pacemaker package - then this bonding may be carried out by immersing this part in a solution containing the polymer to be bonded and the bonding agent and then by drying said solution, in which case the formation of the polymer film and its bonding to the conductive or
30 semiconductive surface take place simultaneously. When such an immersion operation is not possible, if only because the polymer surface is that of an object already formed, then the bonding may be carried out by coating the polymer surface and the conductive or

semiconductive surface with a bonding agent, then applying one surface to the other and drying the resulting assembly, optionally under reduced pressure and/or in a press or clamped.

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The polymer constituting the polymer surface that has to be bonded may be purely organic or hybrid (i.e. organic/inorganic) and may be a thermoset or a thermoplastic, as long as, in the latter case, it can be dissolved or swollen by a substance that is also a solvent or a swelling agent for the material forming the electrografted organic film.

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Moreover, when the electrografted organic film is itself a polymer film, the polymer constituting the polymer surface that has to be bonded may not only be the same as the polymer constituting this organic film but also one that differs therefrom.

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Appropriate polymers are especially polyethylenes, polypropylenes, polystyrenes, polyacrylonitriles, polysiloxanes, polyesters, such as polylactic acid and polyglycolic acid, polyorthoesters, polycaprolactones, polybutyrolactones, polyacrylics, polymethacrylics, polyacrylamides, epoxide resins, ABS resins, polyvinylchloride, polycarbonate, polytetrafluoroethylene, perfluorinated polyethers, phenoplast resins, polyurethanes, epoxy resins, copolymers thereof and blends thereof.

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Within the context of the present invention, it is preferred to use hotmelt polymers - or thermoplastic polymers - even though thermosetting polymers may also constitute useful candidates.

As regards the material that can form the conductive or semiconductive surface, this may be any known material that has the properties of an electrical conductor or
5 semiconductor, such as metals (noble or otherwise) and metal alloys, silicon, germanium or even gallium arsenide.

The method according to the invention has many
10 advantages.

Specifically, it affords, in the first place, the possibility of bonding a polymer material to a conductive or semiconductive material, i.e. a material
15 having a very high melting point for which there is generally no temperature range permitting thermal bonding to a polymer, polymers for the most part decomposing at the melting point of conductive or semiconductive materials.

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It also affords the possibility of bonding a first conductive or semiconductive material, coated with an organic film, whether electrografted or otherwise, to a second conductive or semiconductive material that is
25 not coated with an organic film. In this case, it is sufficient to pretreat the surface of the second material so as to coat it with an electrografted organic film and then to carry out an operation to bond the two conductive or semiconductive materials
30 together, as described above. As a variant, the bonding operation may be carried out after having not only electrografted an organic film onto the surface of the second conductive or semiconductive material, but also having inserted a polymer film between the organic

films forming the surfaces of the two conductive or semiconductive materials. Thus, when the organic film forming the surface of the first conductive or semiconductive material is itself an electrografted
5 film, two bonded joints according to the invention are produced.

In all cases, it turns out that the best results are obtained when the organic film forming the surface of
10 the first conductive or semiconductive material is an electrografted film, the electrografting making it possible to have stronger interfaces than with the other methods currently available for forming an organic film on a surface.

15 On the basis of the foregoing, the method according to the invention also allows two conductive or semiconductive materials, neither of which is coated with a polymer film, to be bonded together.

20 In particular, it allows a bonded joint to be produced between two materials having very high melting points - this is particularly the case for metals, silicon and germanium - without ever having to carry out a step
25 involving such a high melting point. This advantage may prove to be very useful when two conductive or semiconductive regions belonging to separate and complex objects, certain regions of which are heat-sensitive, have to be bonded together. It also
30 contributes to substantial energy consumption savings being made, since it replaces a bonding operation that has to be carried out at very high temperatures with an electrografting operation, which is carried out at room temperature, and an operation of thermally bonding the

two organic materials, which requires much lower temperatures than the thermal bonding of inorganic materials, or even a cold bonding operation.

- 5 As mentioned above, the organic film electrografted onto the conductive or semiconductive surface may or may not be formed from the same polymer as that forming the polymer surface to which said conductive or semiconductive surface is intended to be bonded.

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- In the case when the polymers are the same, the method according to the invention allows thick to very thick films to be obtained very easily on a conductive or semiconductive material, particularly macroscopic films (i.e. those with a thickness of greater than 500 μm) that are highly adherent, whereas electrografting alone results in the formation of films having a thickness not exceeding the order of one micron. The films thus obtained may, for example, be plastic films produced by extrusion or any other means, which are then bonded to the conductive or semiconductive material onto which a film of the same nature has been electrografted beforehand.

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- 25 If the polymers are different, the method according to the invention makes it possible to obtain, on a conductive or semiconductive surface, a polymer film which normally would be unable to be electrografted onto this surface or could only be so with serious difficulties. This is because electrografting is a complex process that does not permit all the polymers to be grafted with the same effectiveness onto all conductive or semiconductive surfaces. In addition, certain polymers, such as those obtained by

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polycondensation of monomers, lend themselves poorly to electrografting. The method according to the invention offers a solution to this problem since all that is required is to electrograft, onto the conductive or
5 semiconductive surface, a polymer film which is both compatible with the polymer with which it was initially sought to coat this surface and is easy to electrograft onto said surface.

10 In all cases, the method according to the invention makes it possible to create very strong adhesive links between the bonded surfaces.

In addition to all the abovementioned advantages, the
15 method according to the invention also has other advantages, in particular the following:

- it does not require any prior modification, and especially no prior functionalization, of the polymer surface that has to be bonded, thereby, in the
20 case of a biocompatible polymer, eliminating the risk of it losing its biocompatibility properties,

- it does not use any chemical compound other than the precursor of the electrografted organic film and, when appropriate, the bonding agent, which
25 considerably limits the risks of toxicity in the case of biomedical applications, and

- it is simple to implement and requires neither complex and expensive operating protocol nor
30 complex and expensive equipment.

Consequently, the method can be used in very many applications, among which mention may be made of the manufacture and renovation of composites intended for the aerospace, aeronautical, automotive, biomedical,

electronic and microsystems industries, the manufacture of implantable surgical and medical instruments, the assembly of sensitive components of microsystems and the packaging of microsystems.

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The subject of the invention is also a structure comprising a conductive or semiconductive surface bonded to a polymer surface via an organic film with a thickness of less than 1 μm .

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Yet another subject of the invention is a structure comprising a conductive or semiconductive surface bonded to a polymer surface via an organic film, in which said organic film is bonded to said conductive or

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semiconductive surface via covalent bonds.

Such structures are, for example, implantable surgical or medical devices such as stents, aneurysm guides, catheter guides, pacemakers, hip prostheses, cochlear

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implant electrodes, dental implants or even electrophysiology electrodes, or else microsystems such as microsensors.

Apart from the above provisions, the invention also

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includes other provisions that will become apparent from the rest of the description that follows, which relates to illustrative examples of bonded joints formed by the method according to the invention and examples of their performance, this description being

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given purely by way of illustration but implying no limitation, with reference to the appended drawings.

Brief description of the drawings

- Figure 1 corresponds to two photographs, respectively A and B, taken in an optical microscope at two different magnifications (50X and 100X), showing the contact region between a gold wire and a gold slide that are bonded together by hotmelt bonding according to the invention.
- 10 Figure 2 corresponds to two photographs, respectively A and B, showing the bonding region between a polystyrene film and a stainless steel strip that are bonded together by hotmelt bonding according to the invention.
- 15 Figure 3 is a photograph illustrating the capability of a hotmelt bonded joint produced according to the invention between two stainless steel strips to withstand an attempt to separate these two strips.
- 20 Figure 4 shows the pentoxifylline release profiles obtained for two polylactic acid (PLA) films filled with 20% and 40% (w/w) pentoxifylline respectively and bonded, by bonding according to the invention, to stainless steel strips (curves 2 and 3), and the profile obtained for a PLA film filled with 20% (w/w) pentoxifylline and having been deposited on a stainless steel strip (curve 1).
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- Figure 5 shows the spectrum, obtained using infrared reflection absorption spectroscopy (IRRAS), of a polyorthoester (POE) film deposited on a stainless steel strip and having a thickness of 500 nm.
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Figure 6 shows the erosion profiles of a POE film bonded by bonding according to the invention to a stainless steel strip (curve 2) and of a POE film deposited on a stainless steel strip (curve 1).

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Example 1: Bonding by hotmelt bonding of a gold wire to a gold slide

10 Butylmethacrylate (BuMA) was dissolved, in a three-electrode electrochemical cell, in a solution comprising 5×10^{-2} mol/l of tetraethylammonium perchlorate in dimethylformamide (DMF), in an amount of 5 mol of butylmethacrylate per liter of solution.

15 Next, a glass slide coated with an evaporated gold layer was immersed in this solution. This slide was connected to the working terminal of a potentiostat and acted as working electrode. The other two electrodes of the device were a large platinum electrode, serving as
20 counterelectrode, and a silver wire used as reference electrode.

Next, ten potential scans were applied to the gold slide under voltammetric conditions, between -0.1 and
25 -2.6 V/(Ag⁺/Ag), at a rate of 100 mV/s. The slide was rinsed with DMF and then with acetone, and finally dried in a stream of argon. A film of polybutylmethacrylate (poly-BuMA) approximately 50 nm in thickness was thus obtained.

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The same treatment was applied to a gold wire 25 μ m in diameter and 3 cm in length. IRRAS spectroscopy was used to check that the wire was actually coated with

poly-BuMA, but its precise thickness was difficult to determine.

5 The wire was then deposited on the slide and held in place by means of a Mohr clamp. The assembly was placed overnight in an oven heated to 200°C, this representing a temperature well below the melting point of gold (1064.43°C).

10 After cooling and removal of the Mohr clamp, it was found that the gold slide could be picked up by merely taking hold of the wire, proving that the bond established between this slide and the wire was strong.

15 Figure 1 shows two photographs taken under the optical microscope at regions where the hotmelt bonding between the wire and the slide are apparent, photograph A corresponding to a magnification of 50X and photograph B corresponding to a magnification of 100X.

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This figure shows that the number of anchoring points is, however, generally quite small, which is probably due to the fact that the wire is not straight, and is unable to be in contact with the slide over its entire
25 length during the hotmelt bonding.

Example 2: Hotmelt bonding of a polystyrene film to a stainless steel strip

30 A 316L stainless steel strip 10 cm in length and 1 cm in width was dipped into a solution containing 3.125 mol/l of methyl methacrylate (MMA), 10^{-2} mol/l of 4-nitrophenyldiazonium tetrafluoroborate and 2.5×10^{-2} mol/l of sodium nitrate in the DMF. This strip

served as working electrode in a three-electrode arrangement similar to that used in Example 1.

This strip was subjected to a series of fifty potential
5 scans under voltammetric conditions, between -0.1 and
-3.0 V/(Ag⁺/Ag), at a rate of 100 mV/s. The strip was
then rinsed with DMF, then with acetone and finally
dried in a stream of nitrogen. A film of polymethyl-
methacrylate (poly-MMA) approximately 300 nm in
10 thickness was obtained.

Next, a polystyrene film 10 cm in length, 1 cm in width
and 75 μ m in thickness was applied to the entire strip
thus treated. The film was pressed onto the strip at
15 one of its ends using a Mohr clamp, so that the pressed
region measured about 2 cm in length by 1 cm in width.
The assembly was placed in an oven at 200°C for two
days.

20 After cooling and removal of the Mohr clamp, the
polystyrene film was found to be bonded to the
stainless steel strip. In particular, it was found to
be possible to lift up the strip by merely taking hold
of the assembly via the unbonded end of the polystyrene
25 film, as illustrated by photographs A and B in
Figure 2.

**Example 3: Hotmelt bonding of a polystyrene film to a
stainless steel strip**

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Using the same protocol as that described in Example 2,
polystyrene films 75 μ m in thickness were bonded to
316L stainless steel strips pretreated by
electrografted films of polymethacrylonitrile (PMAN),

polyhydroxyethyl methacrylate (PHEMA) and poly- ϵ -caprolactone (PCL) respectively, having thicknesses of between 300 and 500 nm.

5 Results similar to those reported in Example 2 were observed, namely the fact that the bond between the polystyrene films and the strips was sufficiently strong for them to be able to be lifted up by taking hold of the assemblies via the unbonded end of these
10 films.

Example 4: Hotmelt bonding of two 316L stainless steel strips

15 Two 316L stainless steel strips 10 cm in length and 1 cm in width were pretreated, in an identical manner, with an electrografted poly-MMA film approximately 300 nm in thickness using a protocol similar to that described in Example 2.

20 One strip was superposed on the other and, inserted between them, at one of their ends, was a polystyrene film 2 cm in length, 1 cm in width and 75 μ m in thickness. The sandwich thus obtained was clamped, using a G-clamp, over an area measuring about 2 cm in
25 length by 1 cm in width.

The assembly was placed in an oven at 200°C for two days.

30 After cooling and removal of the G-clamp, it was observed that the two strips were bonded together. The assembly was placed on the edge and the two unbonded ends of the two strips were separated. A spacer was

inserted into the space thus made so as to maintain a separation of 1 cm between the unbonded ends of the strips. Figure 3 shows that the bonded joint did not fail when stressed in this way.

5

Example 5: Cold bonding of a polylactic acid film to a 316L stainless steel strip

10 This example illustrates the benefit provided by cold bonding, carried out using the method according to the invention, between a polylactic acid (PLA) film and a 316L stainless steel surface, on the stability of the interface resulting from such bonding.

15 This benefit was demonstrated by cold bonding two PLA films, one filled with 20% (w/w) pentoxifylline and the other with 40% (w/w) pentoxifylline, to two 316L stainless steel strips pretreated with an electrografted poly-BuMA film, and by comparing the
20 amount of pentoxifylline released by these films, when the strips were maintained for several days in an aqueous solution, with the amount released by a film of PLA filled with 20% (w/w) pentoxifylline, said film having been deposited on a 316L stainless steel strip
25 that had not been pretreated with an electrografted poly-BuMA film.

To do this, a poly-BuMA film approximately 300 nm in thickness was electrografted onto two 316L stainless
30 steel strips 10 cm in length and 1 cm in width, using the same operating protocol as that described in Example 2.

Moreover, a 10% (w/w) solution of polylactic acid [poly(2-hydroxypropionic acid)], with a weight-average molecular weight of 250,000 g/mol, in chloroform was prepared, chloroform being a solvent for PLA. Starting
5 from this solution, two PLA solutions containing 20% and 40% (w/w) pentoxifylline respectively were prepared. These solutions were stirred for two hours and then a PLA film filled with 20 or 40% (w/w) pentoxifylline was deposited on the stainless steel
10 strips coated with poly-BuMA electrografted by dipping these strips into said solutions. The films thus obtained had a thickness of about 3 μ m. The 316L stainless steel strip not pretreated with an electrografted poly-BuMA film was also immersed in the
15 20% (w/w) pentoxifylline solution.

The strips thus prepared were put in an oven at 40°C for 4 h. Each of them was then introduced into a closed container, containing aqueous PBS buffer solution at
20 7.4 pH and placed in an incubator at 37°C with stirring.

Regular samples were taken from the aqueous solution in which each strip was immersed, said solution being
25 replenished at the same time. Each sample was extracted with chloroform and the pentoxifylline concentration present in the solution was determined by UV-visible spectroscopy in transmission at 278 nm.

30 The results obtained are illustrated in figure 4, in which the cumulative concentration (in percent) of pentoxifylline released is plotted on the Y-axis and time (in hours) is plotted on the X-axis, curves 1, 2 and 3 corresponding, respectively:

- Curve 1, to the PLA film filled with 20% (w/w) pentoxifylline deposited on the untreated stainless steel strip;
- Curve 2, to the PLA film filled with 20% (w/w) pentoxifylline bonded to one of the two stainless steel strips pretreated with an electrografted poly-BuMA film; and
- Curve 3, to the PLA film filled with 40% (w/w) pentoxifylline bonded to one of the two stainless steel strips pretreated with an electrografted poly-BuMA film.

This figure shows that release of pentoxifylline by the PLA film deposited on the unpretreated stainless steel strip is rapid, since a plateau is reached after 8 to 10 days of incubation, indicating this release has stopped. Inspection of that strip showed that the PLA film had delaminated and no longer adhered to the stainless steel surface.

20

Curves 2 and 3 show that, after a very rapid "burst" of release due to diffusion of the excess pentoxifylline, the release profiles for pentoxifylline released by the PLA films bonded to the stainless steel strips pretreated with an electrografted poly-BuMA film become linear and ensure steady delivery of this compound. Inspection of these strips showed, moreover, no local deterioration (for example flaking) of the PLA films. This means that the PLA/poly-BuMA interface was strong enough to withstand the release medium and suggests that release would be only due to progressive hydrolysis of the PLA at its surface in contact with the aqueous solution.

30

Moreover, this example demonstrates that the method according to the invention makes it possible for a biocompatible polymer film such as PLA to be firmly attached to a metal surface without having to modify
5 this polymer beforehand - thereby eliminating any risk of impairing its biocompatibility - and, in addition, of including in this film a fragile molecule, such as pentoxifylline, which is very sensitive to heat and to temperature.

10

It follows that the method according to the invention can be very useful for coating surgical or medical instruments, and especially implants, with biocompatible materials, and in particular with
15 materials intended for the controlled release of biologically active substances.

Example 6: Cold bonding of a polyorthoester (POE) film to a 316L stainless steel strip

20

This example also illustrates the benefit provided by cold bonding, carried out by the method according to the invention, between a polyorthoester (POE) film and a 316L stainless steel surface, on the stability of the
25 interface resulting from such bonding.

This benefit was demonstrated by cold bonding a POE film to a 316L stainless steel strip precoated with an electrografted poly-BuMA film and by comparing the
30 erosion of this film, after the strip was held for several days in 9 g/l aqueous sodium chloride solution at 37°C, with respect to that of a POE film deposited on a stainless steel strip not pretreated with an electrografted poly-BuMA film.

To do this, an approximately 300 nm thick poly-BuMA film was electrografted onto a 316L stainless steel strip 10 cm in length and 1 cm in width using the same
5 protocol as that described in Example 2.

Moreover, a POE₉₅LA₅ (M_w : 60 000; M_n : 38 000; T_g : -14°C), which is a solid POE, was prepared as described by M.B. Sintzel et al. (*Biomaterials*, 19, 791, 1998) [15].

10

Next, a 5% (w/w) POE solution in tetrahydrofuran (THF) was prepared, THF being in fact a solvent for the POE and a swelling agent for the poly-BuMA. A POE film approximately 500 nm in thickness was deposited, by
15 immersing it in this solution, on the stainless steel strip coated with the electrografted poly-BuMA film and on stainless steel strip not pretreated with an electrografted poly-BuMA film.

20 The strips were dried in an oven at 40°C for 6 h. They were then left to incubate according to the same protocol as that described in Example 5.

Periodically, the strips were removed, drained and
25 dried in a stream of argon, and the erosion of the POE films coating these strips was assessed by monitoring the change in the transmittance of the 1745 cm⁻¹ band corresponding to the carbonyl groups of the POE, as measured by IRRAS spectroscopy as a function of time.

30

Figure 5, which shows the IRRAS spectrum of a POE film 500 nm in thickness (i.e. the initial thickness of the POE films used in the present example) deposited on a stainless steel strip, shows the POE carbonyl group

band located at a wavenumber of 1745 cm^{-1} and used for monitoring the erosion of the POE films.

Figure 6, in which the transmittance (in percent) of the carbonyl group band is plotted on the Y-axis and time (in days) is plotted on the X-axis, represents the erosion profile of the POE film bonded to the stainless steel strip pretreated with an electrografted poly-BuMA film (Curve 2) and that of the POE film deposited on the unpretreated stainless steel strip (Curve 1).

This figure shows that the POE film deposited on the untreated stainless steel strip is released very rapidly from the surface of this strip. This is in agreement with inspection of the strip, which showed that this film had been delaminated.

In contrast, no deterioration of the POE film bonded by cold bonding to the strip pretreated with an electrografted poly-BuMA film was observed. Progressive disappearance by hydrolysis in contact with the aqueous solution was simply observed.

These results confirm, should it be necessary, those obtained above in Example 5.

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